High resolution study of low-lying correlation satellites below 25 eV in xenon probed by pulsed-field-ionization-zero-kinetic-energy photoelectron spectroscopy

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High Resolution Study of Low Lying Correlation Satellites in Xenon

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The technique of pulsed field ionization–zero kinetic energy photoelectron spectroscopy, typically applied to the investigation of ionic states of atoms and molecules resulting from single electron excitation, has been used to probe the correlation satellite states of xenon between 23.6–24.7 eV. The resulting spectra show the formation of clearly resolved satellite states with intensities of a similar magnitude to that of the $5s5p^6\,^2S_{1/2}$ ionic state. This technique can be extended to other atomic and molecular species to obtain the positions and cross sections for the formation of such states. [S0031-9007(97)05035-7]

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As the energy of light incident upon an atom or molecule is increased above that of the lowest ionization energy, a variety of neutral and ionic electronic states can be formed. The former include singly excited states converging onto an ion state with one hole in an inner orbital and doubly excited states converging onto an ionic (satellite) state with two electrons excited from the neutral configuration. These neutral resonances may decay to lower-lying ionic states through the process of autoionization. The ionic states include single hole and satellite ionic states formed directly in conjunction with a free electron. Probing the formation and characteristics of these ionic states is a primary aim of photoelectron spectroscopy. In traditional photoelectron spectroscopy the photon energy is scanned, and all electrons formed with a specific kinetic energy and angular distribution are detected. Threshold photoelectron spectroscopy uses static electric fields to allow the selective detection of electrons with near-zero kinetic energy formed in conjunction with a cationic state. Satellite states can be difficult to probe using this technique; in general, such states are formed at high photon energies, they produce low signal intensities and they contribute to a highly congested spectrum. Further, in order to discriminate against the formation of states through nearby autoionizing resonances that result in nonthreshold electrons, there is a need for a high degree of rejection of such electrons, and the effectiveness with which this is accomplished depends upon the electron optical properties of the analyzer, lenses, and electrode surfaces. Separation of such resonant from nonresonant contributions to the partial cross sections for each ionic state is therefore very difficult, but when achieved can significantly increase our understanding of the dominant processes present within an atom or molecule. The introduction of pulsed field ionization–zero kinetic energy (PFI-ZEKE) photoelectron spectroscopy in recent years [1] has largely overcome this problem and enabled a high-resolution spectroscopic probe of ionic states formed by excitation and subsequent field ionization.

The formation of singly excited neutral or ionic states may be understood by invoking the single-particle model while formation of neutral doubly excited or satellite states is forbidden within this approximation and is solely the result of the correlated motions of electrons within the species. It has been useful in the past to separate the correlation effects that result in the formation of satellite states into "intrinsic" and "dynamic" in regard to their threshold behavior [2] and deducing from this behavior the dominant correlations contributing to the intensity of a given satellite.

Intrinsic correlations, which include ground state correlations and virtual Auger processes, are those that exist even in the absence of the photon and are therefore, to a first approximation, independent of the kinetic energy of the outgoing electron. These may be included in a configuration interaction calculation by initial state configuration interaction (ISCI) and final ionic state configuration interaction (FISCI). Dynamic correlations, meanwhile, are those that may show a significant dependence upon the kinetic energy of the outgoing electron. Relaxation or shakeup, conjugate shakeup, and inelastic scattering of the outgoing electron are such examples of dynamical correlations and can be described by FISCI, ISCI, and continuum state configuration interaction (CSCI), or, more generally, interchannel coupling, respectively. Generally, all of the possible CI will be present but in certain cases only some may be dominant. For example, while shakeup dominates at high kinetic energy, conjugate shakeup and inelastic scattering show an enhancement near threshold, and interchannel coupling is expected to exhibit a resonance structure [2].

Calculations beyond the single-particle approximation in xenon that predict satellite positions and intensities are particularly challenging due to large relativistic effects and strong mixing between configurations. The Xe satellite spectrum has previously been measured over a wide incident photon energy range from the near-threshold [3] to the x-ray [4] regions using traditional

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photoelectron spectroscopy, and the partial strengths of various ionic states have been obtained. Formation of an ionic state with one hole in its core results in a "main line" peak at a specific energy in the photoelectron spectrum, while formation of a satellite state results in a peak on the low kinetic energy side of a main line peak. The resolution with which low-lying satellite states have been observed is typically 50 meV at photon energies of 40.8 eV [5], 130 meV at energies less than 100 eV [6], and 300 meV at 1.487 keV [4]. In the region containing the lowest-lying satellite states of xenon, eight ionic states are known to exist from 23.6–24.7 eV, with some separated by an energy as small as 5 meV [7]. Obtaining the partial strengths of each ionic state at any photon energy is therefore often complicated by the fact that there are many unresolved satellite states belonging to different symmetry manifolds within the spectra. A high-resolution light source and detection technique is required to unambiguously determine partial strengths for each ionic state formation at a particular photon energy.

The technique of PFI-ZEKE photoelectron spectroscopy in conjunction with laser sources with repetition rates of <50 Hz employs a delay between the excitation light pulse and the ionization electric field pulse of typically a few μs, allowing effective discrimination against prompt electrons formed in the interaction region and resulting in selective observation of the cation state of interest [8]. Such practical laser sources, though, are currently limited to energy ranges up to ≈ 19 eV [9] and thus detect only the formation of cations in their lower electronic states. A spectrometer at BESSY has recently been developed in which the formation of satellite states in nitrogen [10] and argon [11] with resolutions of 10 and 40 meV, respectively, have been detected. We report the use of a high resolution spectrometer at the Chemical Dynamics Beamline [12] at the Advanced Light Source (ALS) to detect and obtain the relative intensities of formation of the $5s$ main line peak and seven satellite states of xenon.

The spectrometer has been discussed in detail elsewhere [12] and so only an outline will be given here. The atomic beam was formed by a supersonic expansion of 99.999% (research grade) xenon at a stagnation pressure of ≈ 500 Torr through a metal nozzle of 0.127 mm diameter at 298 K. The ALS was operated in a multibunch mode, with 304 light bunches within 608 ns followed by a dark gap of 48 ns, forming one ring period. As the photon energy was scanned across high-lying states that converge to an ionic state, Rydberg states of xenon containing one highly excited electron were formed. Below the threshold for the $5s^{-1}$ state at 23.397 eV these Rydberg states were singly excited, and below each threshold for satellite formation [e.g., the $5s^2 5p^4 ({}^3P) 6s\, {}^4P_{5/2}$ ion state at 23.669 eV] they were doubly excited states containing one high-lying electron. During every alternate dark gap, a 40 ns pulsed electric field of 0.67 V/cm was applied to the interaction region, field ionizing those states formed within ≈ 4 cm^{-1} of an ionic limit [13] and accelerating the resulting near-threshold electrons towards a tandem steradiancy hemispherical analyzer for selective detection.

The photon energy was scanned across the $5s$ main line state and seven of its correlation satellite states from 23.6–24.7 eV in steps of 0.5 meV with a resolution of 1.5 meV. Once detected, each individual line was repeatedly sampled with steps of 0.2 meV and a photon resolution of 0.7 meV. By calibrating the photon energy scale using the ionization onsets of neon and helium, the positions of the lines were found to be at their expected positions within experimental uncertainty (≈ 0.5 meV) and more exact energy calibration was done by comparison with the known optical data [7].

Figure 1 shows a split energy scale spectrum of the observed ionic states formed due to PFI in xenon. Within the energy range sampled, the $5s$ main line peak (the $5s5p^6\, {}^2S_{1/2}$ state) and seven of the eight known satellite peaks were observed. We did not observe the $5s^2 5p^4 5d\, {}^4F_{9/2}$ state and conclude its intensity is less than that of the observed $5s^2 5p^4 5d\, {}^4D_J$ states. The states are labeled with the more familiar LS designations although it is noted that one could alternatively use jK designations. Hansen and Persson have calculated the purity of these ionic states under both coupling schemes [7], and the average purities do not differ significantly.

An expanded view of the observed $5s^2 5p^4 5d\, {}^4D_J$ states is given in Fig. 2, which shows a full width at half-maximum of 0.9 meV. The intensities of all peaks have been calculated by computing the areas under the peaks after correcting for the background and are displayed (relative to the $5s5p^6\, {}^2S$ main line peak with magnitude 100) in Table I. The experimental error in each satellite intensity, due to variations in conditions and statistical fluctuations, is estimated to be from 20% to 30%, with the higher values for the less intense peaks. To allow for light intensity fluctuations the normalized spectra have been

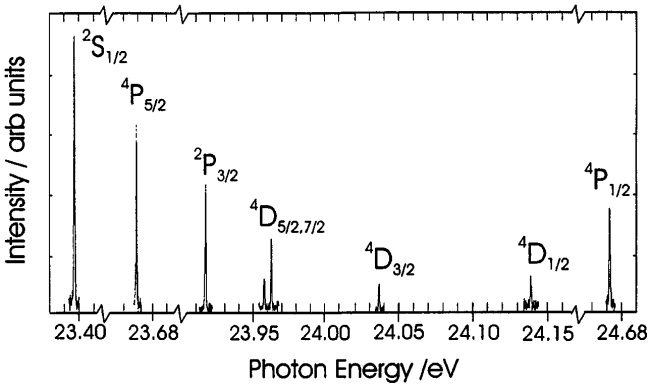

FIG. 1. A split-energy spectrum with consistent energy scale, normalized by photon flux, of the ionic states in xenon observed through PFI-ZEKE photoelectron spectroscopy. The main line state at 23.397 eV and seven correlation satellites are shown. The position of each peak is calibrated from the analysis by Hansen and Persson [7] and labeled with LS notation (see text).

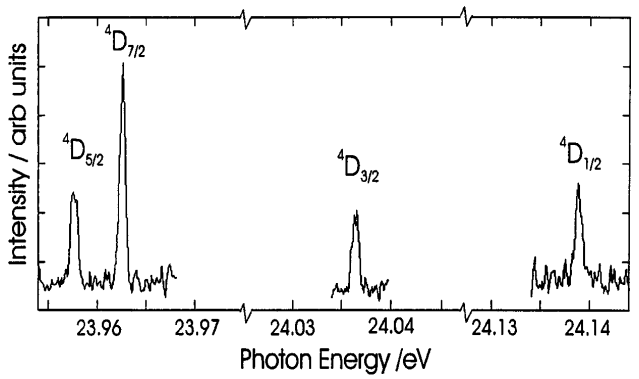

FIG. 2. A split-energy spectrum with consistent energy scale, normalized by photon flux, of the four satellite states belonging to $5s^2 5p^4 5d\,^4D_J$ manifold, showing the width of each peak to be 0.9 meV.

used, although it is possible that conditions such as variations in beam profile can cause minor discrepancies in the data. To minimize this effect several data sets were taken and included in the analysis. For comparison, the reported relative peak heights of these satellite states formed from unpolarized He II α light at 40.8 eV [5] and polarized synchrotron light at 63.5 eV [14] are shown in Table I. It should be noted that the former is not taken at the magic angle with respect to the beam (see [6] for details) and thus could show a maximum difference by a factor of 4 from the true relative cross sections of some states. Also shown are the absolute partial ionization cross sections of the satellites, calculated from our intensity data. These were obtained by scaling the $5s$ photoionization cross-section data of Samson and Gardner [15] which was recorded at photon energies down to 23.6 eV and shows a leveling off towards threshold.

The process which has been observed is one of single or double excitation to a Rydberg state and the subsequent removal of the Rydberg electron by the pulsed electric field. Unlike threshold photoelectron spectroscopy, there is no necessity to find the transmission function of the spectrometer for deconvolution of the data, as all electrons formed through the pulsed field ionization process have the same kinetic energy distribution. Because of the continuity of oscillator strength, the cross section for excitation and the subsequent removal of the outer electron below threshold is expected to develop smoothly into the partial ionization cross section above threshold. Provided there is neither resonant enhancement of the initial (singly excited or doubly excited) Rydberg state nor state-dependent decay or stabilization mechanisms, the relative intensities of the PFI-ZEKE peaks will correspond to the relative partial cross sections for the formation of the corresponding ionic states at threshold. The observed resonances in xenon in this energy range, most of which are sharp, have an average separation of $\approx$40 meV [16]. In general, it is unlikely that a state with the correct symmetry will significantly enhance the excitation to any of the Rydberg neutral states. In considering possible state-dependent decay or stabilization effects, it is noted that the decay paths of the Rydberg states are either by radiation, collisional ionization, or autoionization. Within 4 cm^{-1} of an ionization limit, the principal quantum number of a Rydberg electron is $\gtrsim$165 and the radiative lifetime for singly excited Rydberg state with these values of n is expected to be in the millisecond range [13], significantly longer than the delay time between ionizing pulses (1.3 μs). Within the waiting period, it is highly likely the excited core will fluoresce, but this has been shown to have little effect in other species on high-principal, quantum number Rydberg states [17]. The effect of collisional ionization is expected to be largely independent of the particular state formed, although studies on argon at the first and second ionization thresholds have demonstrated noticeable ion density effects, showing a decay of states with high n and a stabilization of states with low n for spectra taken at high

TABLE I. Intensities and cross sections of nine of the ionic states of xenon with binding energies in the range of 23.3–24.7 eV observed at the thresholds, at 40.8 and 63.5 eV.

Ion state[a]	Energy[b] (eV)	Relative intensities[c] At threshold (this work)	At 40.8 eV[d] (Ref. [5])	At 63.5 eV (Ref. [14])	Cross section At threshold[e] (Mb)
$5s5p^6(^2S_{1/2})$	23.3967	100	100	100	0.50
$(^3P)6s(^4P_{5/2})$	23.6689	54	0.21	...	0.27
$(^3P)6s(^2P_{3/2})$	23.9164	55	0.76	0.2	0.28
$(^3P)5d(^4D_{5/2})$	23.9576	15	0.52	...	0.08
$(^3P)5d(^4D_{7/2})$	23.9627	24	0.09	...	0.12
$(^3P)5d(^4D_{3/2})$	24.0366	9.2	0.58	...	0.05
$(^3P)5d(^4D_{1/2})$	24.1388	12	0.23	...	0.06
$(^3P)5d(^4F_{9/2})$	24.4546	...	0.74	0.2	...
$(^3P)6s(^4P_{1/2})$	24.6719	47	2.4	4.8	0.24

[a] States given in *LS* notation. The parental configuration of the satellite states is $5s^2 5p^4(^3P)$.
[b] Ref. [7].
[c] The intensity for the $5s^{-1}$ main line is arbitrarily normalized to 100.
[d] Data not taken at the magic angle (see text).
[e] Scaled from the data for threshold formation of the $5s^{-1}$ state from Samson and Gardner, Ref. [15].

ion densities relative to those obtained at lower densities [18]. The ion density in our experiment is approximately 200 cm^{-3}, significantly lower than those investigated by Martin *et al.* [18]. A discussion on the observed lifetimes of doubly excited species with one highly excited electron has been recently presented for helium, where long lived neutral excited species of unknown identity were observed close to the He^+ ($N = 1, 2, 3, 4$) thresholds [19].

At threshold, it is apparent that satellite states with high and low J values are formed with equal preference. All such states have intensities not dissimilar to that of the main line peak with those containing the same ionic core having similar intensities. The first two characteristics are noticeable in the lower resolution threshold spectrum of Hall *et al.* [3], but more detailed comparisons with their work are complicated by both the number of unresolved states within and possible resonant enhancements contributing to their spectrum.

The trend from low to high photon energies, with the dominant correlations expected to change, can be seen clearly in Table I. The results at 40.8 and 63.5 eV are expected to be intermediate between the two extremes, where most states have not reached their high energy limits and others have already subsided in intensity from their threshold values. Indeed, by 72 eV, data presented by Lagutin *et al.* [6] show the majority of states observed with binding energy from 23–34 eV correspond to $J = 1/2$ and $\beta \approx 2$, indicating a strong contribution from the $5s^{-1}$ main line. This becomes more extreme at still higher photon energies, and in the x-ray region states with $J = 1/2$ are exclusively observed [4].

Previous calculations of satellite intensities in xenon include those valid at high energy by Hansen and Persson [7], in which the sudden approximation was invoked for ionic states with $J = 1/2$, and the multichannel multiconfigurational Dirac-Fock calculations of Tulkki [20] who reports cross sections that start 4.31 eV above the $5s$ threshold. The CI/perturbation theory approach of Lagutin *et al.* [6] predicts the intensity of the $5s^2 5p^4 6s\,^4P_{1/2}$ state to be $\approx 7\%$ of the main line peak near their respective thresholds. This differs by a factor of 7 from the experimental results of both Hall *et al.* [3] and ourselves. It is our hope that the results presented here will initiate more quantitative studies in the low energy region.

In summary, we have verified the positions and made the first determination of the relative intensities of the seven observed xenon correlation satellites formed at threshold between 23.6–24.7 eV. The high resolution obtained has allowed determination of the absolute partial cross sections and provides a stringent test for the comparison of theoretical predictions. We expect such studies to be extended to the investigation of a variety of atomic and molecular systems, and to higher-lying satellite states, in the near future.

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[1] K. Müller-Dethlefs and E. W. Schlag, Annu. Rev. Phys. Chem. **42**, 109 (1991).
[2] U. Becker and D. A. Shirley, Phys. Scr. **T31**, 56 (1990).
[3] R. I. Hall *et al.*, J. Phys. B **23**, 4469 (1990).
[4] S. Svensson *et al.*, J. Electron Spectrosc. Relat. Phenom. **47**, 327 (1988).
[5] M. Carlsson-Göthe, P. Baltzer, and B. Wannberg, J. Phys. B **24**, 2477 (1991).
[6] B. M. Lagutin *et al.*, J. Phys. B **29**, 937 (1996).
[7] J. E. Hansen and W. Persson, Phys. Scr. **36**, 602 (1987).
[8] *High Resolution Photoionization and Photoelectron Studies*, edited by I. Powis, T. Baer, and C. Y. Ng, Wiley Series in Ion Chemistry and Physics (Wiley, Chichester, 1995).
[9] J. W. Hepburn, in *Laser Techniques in Chemistry*, edited by A. B. Myers and T. R. Rizzo (Wiley, New York, 1995).
[10] F. Merkt and P. M. Guyon, J. Chem. Phys. **99**, 3400 (1993).
[11] B. Krässig *et al.*, J. Phys. B **29**, L449 (1996).
[12] C.-W. Hsu *et al.*, Rev. Sci. Instrum. **68**, 1694 (1997); C.-W. Hsu *et al.*, J. Chem. Phys. **106**, 8931 (1997).
[13] *Rydberg States of Atoms and Molecules*, edited by R. F. Stebbings and F. B. Dunning (Cambridge University Press, Cambridge, England, 1983).
[14] A. Kikas *et al.*, J. Electron Spectrosc. Relat. Phenom. **77**, 241 (1996).
[15] J. A. R. Samson and J. L. Gardner, Phys. Rev. Lett. **33**, 671 (1974).
[16] K. Codling and R. P. Madden, J. Res. Natl. Bur. Stand., Sect. A **76A**, 1 (1972).
[17] W. Kong, D. Rogers, and J. W. Hepburn, Chem. Phys. Lett. **221**, 301 (1994).
[18] J. D. D. Martin, C. Alcaraz, and J. W. Hepburn, J. Phys. Chem. **101**, 6728 (1997).
[19] E. Sokell *et al.*, J. Phys. B. **29**, L863 (1996).
[20] J. Tulkki, Phys. Rev. Lett. **62**, 2817 (1989).